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III. "Further Remarks on the Organo-metallic Radicals Mercuric, Stannic, and Plumbic Ethyl."—No. III. By GEORGE BOWDLER BUCKTON, Esq., F.R.S., F.L.S., F.C.S. Received March 3, 1859.

(Abstract.)

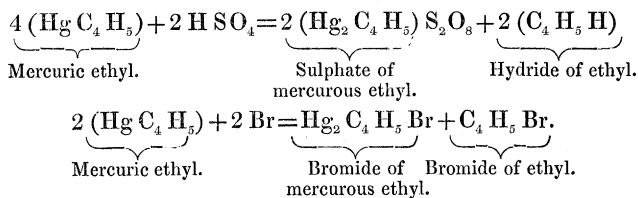
On resuming my inquiries into the nature of these organo-metals, I have met with some interesting reactions, which I here wish briefly to notice.

The preparation of mercuric, stannic, and plumbic ethyls, through the action of zinc ethyl on various organic and inorganic salts, has been already detailed in my sketch published in the 'Proceedings of the Royal Society*'; but at that time, I was not able to fix, with certainty, the constitution of the compounds which were produced by acids on the different radicals. An appeal to analysis now enables me to state the following

Mercuric ethyl.

The reactions of this liquid are well-marked. Towards sulphuric and hydrochloric acids it follows the deportment of its homologue mercuric methyl. When assisted by gentle heat, one equivalent of ethyl is disengaged, which unites with the hydrogen of the acid, and forms hydride of ethyl, whilst the acid takes its place, and gives rise to the corresponding salt of mercurous ethyl.

The radical bursts into flame when poured into chlorine gas, and is almost entirely destroyed; but when it is slowly mixed under water with iodine or bromine, the disengagement of ethyl gas is scarcely perceived, and iodide or bromide of ethyl may be recovered by distillation.



From considerations connected with the vapour density of mercuric ethyl and mercuric methyl, as given by experiment, there seem to be reasons for believing that the formulæ of all the organo-metals of this

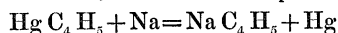
* Proc. Roy. Soc. vol. ix. p. 309.

group should, in correctness, be doubled. I have not, however, yet been able to satisfy these views by direct experiment. Zincethyl acts readily on salts of mercurous methyl; and in all probability gives a body compounded of ethyl and methyl with a double equivalent of mercury $\left. \begin{array}{c} \text{Hg C}_4 \text{H}_5 \\ \text{Hg C}_2 \text{H}_3 \end{array} \right\}$. The substance, however, if produced, is obviously broken by distillation into the two radicals mercuric ethyl and mercuric methyl. Experiment may perhaps prove more successful if salts of stannic methyl be similarly treated.

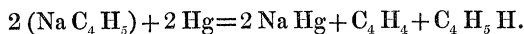
The electro-negative character of the group $\text{C}_{n2} \text{H}_{n2+1}$ in the class of organo-metals to which zincethyl belongs, may now perhaps be considered as established. Some interest, nevertheless, attaches to the question whether sodium is capable of displacing ethyl from mercuric ethyl. An answer to this question would give us some means of judging the position of ethyl, as regards its electro-negative function towards the true metals.

At ordinary temperatures, sodium has only a slow action on mercuric ethyl, but after the lapse of a few hours a voluminous grey sponge is formed, whilst the liquid entirely disappears. This sponge-like body has the property of spontaneous combustibility in a marked degree, and is liable to explosion from apparently very slight causes. By the application of a gentle heat, a strong rush of gaseous matter is evolved which eudiometric experiments proved to be a mixture of ethylene and hydride of ethyl, obviously proceeding from the disintegration of a double molecule of ethyl.

From this experiment we should conclude that ethyl, methyl, &c. in these radicals are still negative to mercury, and therefore, that mercury, copper, &c. would not, as Mr. Wanklyn supposes, displace ethyl in sodiumethyl*. More probably, perhaps, sodiumethyl is first formed in the reaction, and then decomposed by heat



and by heat



The mercury is supposed here to be inert, and in no way to determine the decomposition.

Stannic diethyl.

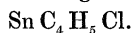
Much of the uncertainty which has attached to some of the for-

* Proc. Roy. Soc. vol. ix. p. 345.

mulæ of the salts of stanethyl, has originated, without doubt, from the mode adopted by Löwig in their elimination. Strecker has lately shown that many of these compounds may, with probability, be referred to the types of the inorganic oxyiodides and oxychlorides of tin.

The following experiments were undertaken with the impression that the pure salts of stanethyl might be more advantageously procured by acting directly on the radical itself.

Stannic diethyl, $\text{Sn}(\text{C}_4\text{H}_9)_2$, like mercuric ethyl, loses one of its equivalents of ethyl when digested with concentrated acids. The action, however, is very slow with hydrochloric acid, an oily body being first formed, possessed of an exceedingly pungent odour; but finally a chloride is obtained having the formula



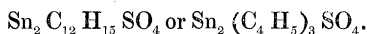
This salt produces fine, hard crystals, which are soluble in water, and, when pure, almost inodorous. A more ready method of obtaining this chloride consists in adding the radical, drop by drop, to a layer of bromine covered with water, until the bromine is decolorized; the aqueous solution is then decomposed by potash, which precipitates oxide of stanethyl in the form of a white powder, from which the pure salts of stanethyl may be readily procured.

The solubility of these salts in aqueous potash has been rather variously stated by Löwig and Frankland, and also their characters as odorous and inodorous. The truth is, that unless the salts of stanethyl are formed from the oxide, they are almost always contaminated with the above-mentioned oily chloride, the oxide of which is soluble in potash. As oxide of stanethyl is not affected by alkaline solutions, these two bodies may be separated without difficulty.

The soluble oxide may be recovered from the alkaline solutions by distillation. It passes over, together with aqueous vapour, in the form of an exceedingly caustic and pungent oil, which blues litmus, and has all the characters of a powerful base. Water dissolves it in moderate quantities, but precipitates it again on the addition of common salt. When deprived of water, the oily base solidifies into a crystalline mass.

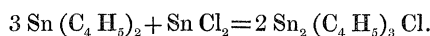
This oxyde forms definite salts with acids, all more or less pungent. With hydrochloric and hydriodic acids, uncrystallizable bodies,

insoluble in water, are produced, but with sulphuric acid it forms fine, colourless crystals, which by analysis gave the formula



For this compound I propose the name of sulphate of distannic triethyl. It has, in a remarkable degree, the unusual property of being more soluble in cold than in hot water. A cold saturated solution becomes semi-solid by raising the temperature somewhat below ebullition.

A consideration of the elements of the above formula furnished an idea of these bodies being either double salts, compounded of one equivalent of stannic diethyl with one equivalent of any salt, $\text{Sn C}_4 \text{H}_5 \text{X}$, or else a combination of three equivalents of stannic diethyl, with one equivalent of an inorganic salt Sn X_2 , resulting in two molecules of the sesqui-ethylated salt. Thus



Experiment proves that the former bodies mix, but do not combine chemically, at any moderate heat. The latter bodies, on the other hand, exhibit strong chemical action, and disengage great heat during combination.

Bichloride of tin forms an oily body with stannic diethyl, chiefly composed of chloride of distannic triethyl, which by treatment with potash may be made to furnish the corresponding salts without difficulty.

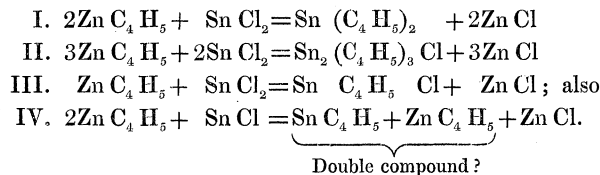
Iodide of distannic triethyl may often be found amongst the products of the action of tin on iodide of ethyl. It is very probably identical with the oil noticed by Riche and Cahours, and described by them as possessing the pungent odour of oil of mustard.

These salts also must be considered to be identical with those described by Löwig under the somewhat inappropriate name of "methylo-stanethyls." The present name is suggested as more in accordance with their true constitution. They finally pass, by the action of zincethyl, into the radical stannic diethyl.

The presence of iodide of distannic triethyl amongst the stannic bodies in Löwig's experiments can be satisfactorily accounted for, by presuming the incomplete reduction of the iodides by the alloy of tin and sodium, employed in the reactions.

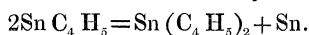
The behaviour of zincethyl towards the chlorides of tin may be

expressed, step by step, by the following equations, the tin-salt being supposed to be added to the zincethyl:—



I have failed in satisfactorily separating the radical stannic ethyl from the excess of zincethyl, as represented in the last reaction. By the addition of water great heat is generated, and tin is thrown down in its metallic state.

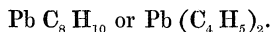
By distillation also, the radical stannic ethyl is similarly broken up,



Plumbic diethyl.

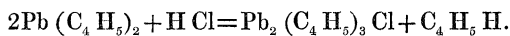
In the abstract above alluded to, I have stated the difficulties which at that time prevented my obtaining the lead radical in a state of purity. This difficulty arises from its tendency to decompose suddenly at a point below that of ebullition. This disadvantage is entirely obviated by conducting the distillation *in vacuo*, or at least under reduced atmospheric pressure. The organo-metal was found to distil unchanged under a pressure of 7·5 inches of mercury at a temperature of 152° C., the barometer at 30·5 inches. This is a remarkable lowering of the boiling-point, which at ordinary atmospheric pressures appears to be a few degrees above 200° C.

Analysis gave numbers leading to the formula—



Plumbic diethyl is a limpid and colourless fluid, possessing a specific gravity of 1·62. It burns with an orange flame, tinged at the edges with pale green, and disengages whilst burning much oxide of lead.

The only salts hitherto prepared from this radical seemed formed on the type of the sesquioxides. By passing excess of hydrochloric-acid gas over the organo-metal, hydride of ethyl is liberated, and chloride of diplumbic triethyl is obtained.



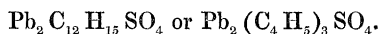
The chloride is a fine crystalline body, occurring in long needles,

which fuse at a gentle heat, and then take fire, with the characteristic lead flame.

Oxide of diplumbic triethyl may be obtained by heating any of the corresponding salts with strong potash, or by acting on a solution of the chloride with oxide of silver. It is a crystalline body, which fuses into an oil-like liquid, at a gentle heat.

Sulphuric acid forms an abundant crop of asbestos-like needles when mixed with a warm solution of the chloride of diplumbic triethyl. It may also be obtained by neutralizing a solution of the oxide, and also by the action of sulphate of silver on the chloride.

Analysis furnished numbers which pointed to the formula



All the salts of this sesqui-ethylated base are volatile, and their vapours attack the eyes and mucous membrane of the throat. In this respect they imitate their homologues in the stannic series.

In concluding this short abstract, I will only express my belief that a wide field of research is still open for inquiry, and that some promising experiments are at present in hand, from the right understanding of which we may hope to throw additional light on these interesting substances.

IV. "On Muscular Action from an electrical point of view."

By CHARLES BLAND RADCLIFFE, M.D., F.R.C.P., Physician to the Westminster Hospital, &c. Communicated by JAMES PAGET, Esq. Received February 6, 1859.

This Paper was read in part.

March 17, 1859.

Sir BENJAMIN C. BRODIE, Bart., President, in the Chair.

The reading of Dr. RADCLIFFE's Paper, "On Muscular Action from an electrical point of view," was resumed and concluded.

(Abstract.)

The author begins by observing, that the signs of electrical action in living muscle die out *pari passu* with the signs of irritability; and, as with these latter signs, *their last trace has disappeared before the occurrence of rigor mortis.*